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<p>(21) International Application Number: PCT/AU87/00344 (22) International Filing Date: 13 October 1987 (13.10.87) (31) Priority Application Number: PH 8726 (32) Priority Date: 28 October 1986 (28.10.86) (33) Priority Country: AU (71) Applicant (for all designated States except US): COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION [AU/AU]; Lime-stone Avenue, Campbell, ACT 2601 (AU). (72) Inventors; and (75) Inventors/Applicants (for US only) : HOUCHIN, Martin, Richard [GB/AU]; 61 Cumberland Road, Pascoe Vale, VIC 3044 (AU). SINHA, Hari, Narayan [AU/AU]; 23 Scheele Street, Surrey Hills, VIC 3127 (AU).</p>		<p>(74) Agent: BERRYMAN, D., W.; Industrial Property Section, ICI Australia Operations Proprietary Limited, P.O. Box 4311, 1 Nicholson Street, Melbourne, VIC 3001 (AU). (81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent), US. Published With international search report.</p>
<p>(54) Title: PROCESS FOR THE PRODUCTION OF ZIRCONIUM SULPHATE</p>		
<p>(57) Abstract</p> <p>A process for the preparation of zirconium sulfate tetrahydrate. This process involves the leaching of a zirconium source with sulfuric acid and the formation of a zirconium sulfate tetrahydrate by the dilution of the slurry produced by the leach. The process further provides for the reconstitution of the acid diluted to produce the zirconium sulfate tetrahydrate once the zirconium sulfate tetrahydrate has been crystallised and removed from the diluted acid. The reconstituted acid is then recycled to the leach step. This process may include various purification techniques. The process allows for the preparation of zirconium sulfate tetrahydrate wherein waste sulfuric acid produced as a byproduct is minimized.</p>		

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PROCESS FOR THE PRODUCTION OF ZIRCONIUM SULPHATE

This invention relates to a process for obtaining zirconium sulfate from zirconiferous materials and is particularly concerned with the production of zirconium sulfate tetrahydrate from caustic-leached-dissociated zircon (CDZ).

5

Production of zirconium in a stable, water soluble form is in demand for coatings, e.g. in the paint industry for protection of TiO_2 , and as a starting material for production of zirconium chemicals. Zirconium sulfate tetrahydrate ($\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) is stable, very water soluble, crystallizes as a pure stoichiometric compound and is easily converted to other zirconium compounds.

10

In International Patent Application No.

15

PCT/AU86/00018 there is described a process for the production of zirconium sulfate, which is based on the finding that the efficiency of sulfuric acid leaching of dissociated zircon can be greatly enhanced if proper attention is paid to the removal from the system of water which is produced during leaching.

20

Said patent application also shows how the initial leach product, can be quantitatively converted to the stable zirconium sulfate tetrahydrate by addition of a measured amount of
5 water. The heat produced by the addition of water to the acid leach slurry aids the dissolution of the zirconium salt thereby allowing the removal of insoluble impurities.
On cooling, the zirconium quantitatively
10 recrystallizes as the hydrated 10 sulfate $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$.

Further, International Patent Application No. PCT/AU86/00162 describes a process based on the finding that low-silica-containing zirconiferous
15 materials, particularly caustic-leached-dissociated zircon (CDZ) can be effectively leached at temperatures in the range 175°C to 250°C using sulfuric acid (preferably at a concentration such that the acid boils at the leaching temperature).

20 As a result of the production of zirconium sulfate tetrahydrate, waste sulfuric acid is produced. We have now found a process for the production of zirconium sulfate tetrahydrate from zirconiferous materials which allows elimination or
25 at least minimization of acid waste. By correct management of reactants and products it is possible, with this process, to establish a balance such that the residual acid is recycled and hence a minimum of acid waste is produced.

30 According to the present invention, there is provided a process for the production of zirconium sulfate tetrahydrate which comprises the steps of:

- (i) leaching a zirconium source with sulfuric acid to produce an acid leach slurry;

- (ii) diluting the resulting acid leach slurry to produce zirconium sulfate tetrahydrate crystals in a diluted sulfuric acid slurry;
- (iii) separating said zirconium sulfate tetrahydrate crystals from the diluted acid;
- (iv) reconstituting the diluted acid to give sulfuric acid of a concentration suitable for use in step (i); and
- (v) recycling the reconstituted sulfuric acid to leach step (i).

It will be understood by those skilled in the art that the temperature at which the zirconium source may be leached is dependent on the concentration of the sulfuric acid. The greater the concentration of the sulfuric acid the higher the boiling point and hence the higher the temperature at which the zirconium source may be leached. The maximum temperature at which the leach can be conducted influences the nature of materials that can be leached.

The concentration of sulfuric for use in the leach at step (i) of the present invention may conveniently be in the range of 65% to 95% w/w sulfuric acid. It is preferred that the concentration of said sulfuric acid is in the range 75% to 90% w/w sulfuric acid. More preferably the concentration of said sulfuric acid is in the range of 80% to 90% w/w sulfuric acid. Most preferable for use in the leach at step (i) of the present invention is 85% w/w sulfuric acid.

In the process of the present invention it has been found that particularly suitable zirconium sources are low-silica-containing zirconiferous materials. The advantage in leaching

5 low-silica-containing zirconiferous materials is that the leach may be carried out at relatively low temperatures, typically in the range of 175°C to 250°C. A particularly advantageous low-silica-containing zirconiferous material is

10 caustic-leached-dissociated zircon.

Thus in one embodiment of the present invention it is preferred that the zirconium source be a low-silica-containing zirconiferous material. More preferably the zirconium source is caustic-

15 leached-dissociated zircon as it allows the acid leach of step (i) to be carried out at a relatively low temperature. This provides some flexibility in the choice of materials of construction that can be used in apparatus of use in the process of the

20 present invention.

It is also preferable in the process of the present invention that the sulfuric acid for use in the leach of step (i) has a composition wherein the boiling point of the sulfuric acid corresponds to

25 the temperature of said leach.

The reconstitution of the diluted acid at step (iv) may conveniently be achieved by the addition of sufficient sulfuric acid at a concentration greater than that of the sulfuric

30 acid for use in the leach at step (i) to reconstitute the diluted acid to the concentration of the sulfuric acid for use in the leach at step (i)..

In one embodiment of the present invention the concentration of the sulfuric acid for use in the leach at step (i), the concentration of sulfuric acid to which the acid leach slurry is
5 diluted at step (ii) and the concentration of the sulfuric acid used to reconstitute the diluted acid at step (iv) may be chosen, having regard to the sulfuric acid balance of the process, to provide a process in which the
10 volume of reconstituted acid that is recycled at step (v) is equivalent to that used in the leach at step (i) thereby providing a process in which waste sulfuric acid is reduced to a minimum.

15 The yield and purity of the zirconium sulfate tetrahydrate crystals and the practical application of the process are determined by a number of inter-related process variables.

1. The concentration at which the zirconium
20 sulfate tetrahydrate crystals are produced at
step (ii).

It will be understood that the zirconium sulfate tetrahydrate is the stable solid phase in equilibrium with sulfuric acid over the approximate
25 concentration range of 30% to 80% w/w sulfuric acid at room temperature.

The solubility of zirconium sulfate tetrahydrate is less than 10 g dm^{-3} (expressed as ZrO_2) at 25°C over the range 45% to 75% w/w H_2SO_4 .
30 Thus during the production of zirconium sulfate tetrahydrate at step (ii) a high yield is obtained if the resulting acid leach slurry from step (i) is diluted to a concentration in said range.

Therefore in a further embodiment of the present invention it is preferred that the zirconium sulfate tetrahydrate is crystallized at step (ii) by diluting the acid leach slurry to a
5 concentration in the range of from 45% to 75% w/w sulfuric acid.

At about 65% w/w sulfuric acid the solubility of the zirconium sulfate tetrahydrate is at a minimum. Hence a maximum yield of zirconium sulfate
10 tetrahydrate crystals may be obtained by diluting the acid leach slurry of step (i) to a concentration of about 65% w/w sulfuric acid.

However the purity of the zirconium sulfate tetrahydrate crystals produced at step (ii) may be
15 increased by diluting the acid leach slurry from step (i) to a concentration wherein the solubility of an undesirable impurity is increased, thus reducing the amount of said impurity in the zirconium sulfate tetrahydrate crystals produced
20 at step (ii).

It will be appreciated that the concentration to which the acid leach slurry of step (i) is diluted in step (ii) may be selected so as to minimise the amount of undesirable impurities and to
25 maximise the yield of zirconium sulfate tetrahydrate.

2. The volume of acid used in the acid leach of step (i)

The fluidity of the acid leach slurry depends
30 on the amount of acid used to leach the zirconium source. The more acid used in the leach the more fluid, or free flowing is the consistency of the acid leach slurry.

Minimizing the amount of acid used in the leach minimizes the amount of dilute acid to be reconstituted and recycled. By minimizing the amount of acid to be recycled, the concentration of the reconstituted acid used for subsequent leaches, and hence the leach temperature, can be maximized. However if the leach product is to be transported to another vessel for subsequent processing, it may be desirable to use additional acid to provide a slurry with a "free-flowing" consistency.

3. The acid content of the zirconium sulfate tetrahydrate crystals separated from the diluted acid at step (iii)

The free-moisture, or free-acid, content of zirconium sulfate tetrahydrate crystals separated at step (iii) also affects the acid recycle balance. Where said crystals are separated in the form of a cake or aggregate free-acid may be held up in the cake or aggregate. Any acid held up in said cake or aggregate is not recycled. Thus the volume of acid to be reconstituted and recycled is decreased. The moisture content of said cake or aggregate is determined by the size, shape and crystal nature of the zirconium sulfate tetrahydrate, the separation technique and apparatus employed.

The zirconium sulfate tetrahydrate crystals may be separated by any convenient method such as, for example, filtration, decanting of the diluted acid or centrifugation.

4. Purification methods

The purity of the zirconium sulfate tetrahydrate crystals may be improved by a number of methods both during the process for the production of the zirconium sulfate tetrahydrate and during the reconstitution and recycle of the sulfuric acid.

If the process of the present invention is to be performed under total acid recycle conditions where no waste acid is produced, then once the process has reached "steady state" in all steps, the purity of the zirconium sulfate tetrahydrate crystals will primarily be determined by the purity of the zirconium source.

If a higher purity product is required further steps may be added to the process to reduce impurities.

Acid insoluble impurities may be reduced in a "hot filtration" step after the dilution and before the cooling and the production of the zirconium sulfate tetrahydrate crystals at step (ii). To perform the "hot filtration" step, sufficient acid must be present to dissolve the initial zirconium sulfate product and retain it in solution long enough to perform the hot filtration.

The dilution of the acid leach slurry at step (ii) generates heat. This in combination with the increased volume may be sufficient to dissolve all, or at least a substantial proportion, of the zirconium sulfate tetrahydrate produced by said dilution. Before the slurry so-produced is allowed to cool acid-insoluble impurities may be removed or reduced by filtration. It will be understood that heat may be supplied by other convenient means to promote the dissolution of the zirconium sulfate tetrahydrate. The dissolution of the zirconium

sulfate tetrahydrate may also be promoted by the addition of further acid of the same concentration as the diluted acid leach slurry. Said addition of further acid may be from a storage reservoir to which said acid is returned after filtration. It will be understood that by returning the volume of acid, that was added to promote the dissolution of zirconium sulfate tetrahydrate, to the storage reservoir the acid recycle balance may be maintained.

Acid soluble impurities may be removed, or reduced, by washing the zirconium sulfate tetrahydrate crystals to remove, or reduce, retained sulfuric acid. The zirconium sulfate tetrahydrate crystals may be washed, for example, with acetone. Acid soluble impurities may also be reduced by "bleeding" the acid recycle stream or by reducing impurities from this stream. Methods for reducing acid soluble impurities from the acid recycle stream may include, for example, precipitation, ion exchange, solvent extraction or any other suitable process.

The process of the present invention is further illustrated and described by the following non-limiting examples:

Example 1

150 g of caustic-leached-dissociated-zircon (CDZ, 95% ZrO_2) was reacted with 491 g of 85% w/w H_2SO_4 (426 g of 98% H_2SO_4 plus 65 g of H_2O) at its boiling point of 225°C for 2.5 hours. The reaction vessel was fitted with a stirrer, a temperature

controller and an air condensor which allowed water produced by the reaction to distill off thereby maintaining constant sulphuric acid concentration and constant temperature. After allowing the
5 reaction moisture to cool to 70°C, 143 g of water was added with stirring, resulting in a temperature rise and dissolution of the initial zirconium sulphate product. On cooling, $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ crystals deposited. The slurry was filtered, giving
10 193 g of filtrate (65% w/w H_2SO_4) and 480 g of moist product (380 g $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, 10 g solid "impurities" and 90 g of 65% H_2SO_4 held in filter cake). This product contained 10 g of water insoluble residue (ZrSiO_4 , SiO_2 and unreacted ZrO_2).
15 The 193 g of 65% w/w H_2SO_4 filtrate was reconstituted with 298 g of 98% H_2SO_4 and recycled for a subsequent leach.

Although initially the product described from the above process was purer than the CDZ feed
20 material, on continued recycling a "steady-state" system is produced where product purity (based on ZrO_2 content) was equal to the feed purity.

Leach efficiency was 98% based on the CDZ feed containing 95% ZrO_2 . Zirconium recovery from
25 the slurry produced by the acid leach was 98%.

Example 2

150 g of CDZ (95% ZrO_2) was reacted with 387g of 85% H_2SO_4 as described in Example 1. After allowing the reaction mixture to cool to 70°C, 100 g
30 of H_2O was added with stirring. Crystals of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ formed almost immediately. This thick slurry was filtered giving 45 g of filtrate (65%

w/w H_2SO_4) and 480 g of moist product as in Example 1. One portion of the filter cake was washed with acetone, then calcined to ZrO_2 for analysis. Another portion was calcined without washing. The products had the following analyses.

Analysis (ppm)	Y	U	Th	Hf	Fe	Ti	Ca	Si	Al
Feed	1170	250	140	1.63%	200	850	200	1.1%	650
10 Washed Product	1160	130	130	1.63%	30	200	28	1.1%	410
Unwashed Product	1150	180	140	1.59%	120	630	83	1.1%	650

Example 3

15 150 g of CDZ (95% ZrO_2) was reacted with 491 g of 85% w/w H_2SO_4 as described in Example 1. After reaction for 2.5 hours, 350 g of 65% H_2SO_4 was added to the reactor from a storage vessel, followed by 143 g of H_2O . The resulting hot slurry was quickly filtered. On cooling the filtrate deposited

20 $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ crystals. The slurry was filtered, giving 543 g of filtrate (65% H_2SO_4) and 470 g of a moist product comprising (380 g of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ and 90 g of 65% H_2SO_4). This product was totally water soluble.

25 350 g of the 65% H_2SO_4 filtrate was returned to storage vessel and 193 g reconstituted with 298 g of 98% H_2SO_4 and recycled for a subsequent leach.

The hot filtration step removes ZrSiO_4 , SiO_2 and unreacted ZrO_2 but very little else. Therefore, as in Example 1 the other impurities will eventually reach a steady-state in the system and then report
5 in the product in the same concentration as they are present in the feed. The product purity can be improved by washing the product filter cake, as in Example 2, by bleeding a portion of the recycled acid (e.g. in the storage vessel) by any suitable
10 technique such as precipitation, ion exchange, solvent extraction etc., of the impurities. Elimination of impurities in the acid recycle line results in product purities similar to those given in Example 2, but with the Si content reduced to
15 near zero (typically 20 ppm) depending on the effectiveness of the hot filtration.

Example 4

150 g of CDZ was reacted with 759 g of 85% H_2SO_4 as described in Example 1. After allowing the
20 reaction mixture to cool to 90°C , 220 g of H_2O was added with stirring. The resulting hot slurry was quickly filtered. On cooling, the filtrate deposited $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ crystals which were filtered, washed with acetone and dried at the pump.
25 Yield = 380 g. The product was totally water soluble. A portion of the product was calcined to ZrO_2 and gave the analysis below.

Analysis (ppm)	Y	U	Th	Hf	Fe	Ti	Ca	Si	Al
30 CDZ Feed	1170	250	140	1.63%	200	850	200	1.1%	650
Product	1140	130	140	1.60%	30	210	25	20	350

The claims defining the present invention are as follows:

1. A process for the preparation of zirconium sulfate tetrahydrate comprising the steps of:
 - 5 (i) leaching a zirconium source with sulfuric acid to produce an acid leach slurry;
 - (ii) diluting the resulting acid leach slurry to produce zirconium sulfate tetrahydrate crystals in a diluted sulfuric acid slurry;
 - 10 (iii) separating said zirconium sulfate tetrahydrate crystals from the diluted acid;
 - (iv) reconstituting the diluted acid to give sulfuric acid of a concentration suitable for use in step (i); and
 - 15 (v) recycling the reconstituted sulfuric acid to leach step (i).
2. A process according to claim 1 wherein the concentration of sulfuric acid for use in the leach at step (i) is in the range of 65% to 95%
20 w/w H_2SO_4 .
3. A process according to either of claims 1 or 2 wherein the concentration of sulfuric acid for use in the leach at step (i) is in the range of 75% to 90% w/w H_2SO_4 .

4. A process according to any one of claims 1 to 3 inclusive wherein the concentration of sulfuric acid for use in the leach at step (i) is in the range of 80% to 90% w/w H_2SO_4 .
- 5 5. A process according to any one of claims 1 to 4 inclusive wherein the concentration of sulfuric acid for use in the leach at step (i) is 85% w/w H_2SO_4 .
- 10 6. A process according to any one of claims 1 to 5 inclusive wherein said zirconium source is a low-silica-containing zirconiferous material.
7. A process according to any one of claims 1 to 6 inclusive wherein said zirconium source is caustic-leached-dissociated zircon.
- 15 8. A process according to any one of claims 1 to 7 inclusive wherein the leach is carried out at a temperature in the range of 175°C to 250°C.
- 20 9. A process according to any one of claims 1 to 8 inclusive wherein said leach is carried out with sulfuric acid at a concentration such that the boiling point of the sulfuric acid composition corresponds to the temperature of said leach.
- 25 10. A process according to any one of claims 1 to 9 inclusive wherein the acid leach slurry produced from step (i) is diluted such that the concentration of sulfuric acid is in the range of 45% to 75% w/w sulfuric acid.

11. A process according to any one of claims 1 to 10 inclusive wherein the zirconium sulfate tetrahydrate crystals are separated at step (iii) by any one of the group consisting of filtration, decanting of the diluted acid and centrifugation.
12. A process according to any one of claims 1 to 11 inclusive wherein the diluted acid is reconstituted at step (iv) by the addition of sulfuric acid at a concentration greater than the concentration of sulfuric acid used for the leach at step (i).
13. A process according to any one of claims 1 to 12 inclusive where in acid insoluble impurities in the zirconium sulfate tetrahydrate crystals produced at step (ii) are reduced by hot filtration after the dilution and before the cooling and production of said crystals.
14. A process according to any one of claims 1 to 13 inclusive wherein acid insoluble impurities in the zirconium sulfate tetrahydrate crystals are reduced by washing.
15. A process according to any one of claims 1 to 14 inclusive where in acid soluble impurities in the reconstituted sulfuric acid are reduced in sulfuric acid recycle stream by removing at least a portion of said impurities.
16. A process according to claim 15 wherein said impurities are reduced by "bleeding" a portion of the recycle stream.

17. A process according to either claim 15 or 16 wherein said impurities are reduced in the sulfuric acid recycle stream by means of precipitation, ion-exchange or solvent extraction.

- 5 18. A process for the preparation of zirconium sulfate tetrahydrate comprising the steps of:
leaching caustic-leached-dissociated zircon with
sulfuric acid at a concentration of between
80% and 90% w/w sulfuric acid at a temperature
10 which corresponds to the boiling point of the sulfuric acid;
diluting the resulting acid leach slurry to a
concentration of 65% w/w H_2SO_4 to
produce $Zr(SO_4)_2 \cdot 4H_2O$ and reducing acid
15 insoluble impurities by hot filtration before the crystallization of zirconium sulfate tetrahydrate crystals;
separating the zirconium sulfate tetrahydrate crystals from the diluted acid leach slurry;
20 washing the zirconium sulfate tetrahydrate crystals with acetone;
reconstituting the diluted acid by the addition of 98% w/w sulfuric acid;
recycling the reconstituted sulfuric acid to the
25 leach step; and
reducing the level of acid insoluble impurities in the sulfuric acid recycle streams by means selected from the group consisting of bleeding a portion of the sulfuric acid stream,
30 precipitation of said impurities, ion exchange solvent extraction of said impurities and combinations thereof.

19. A process according to any one of claims
1 to 18 inclusive wherein the concentration of
sulfuric acid for use in the leach at step
(i), the concentration of sulfuric acid to which
5 the acid leach slurry is dissolved at step (ii)
and the concentration of sulfuric acid used to
reconstitute the diluted sulfuric acid at
10 step (iv) are chosen wherein the volume of
reconstituted sulfuric acid recycled at
step (v) is equivalent to the volume of
sulfuric acid used in the leach at step (i).

20. A zirconium sulfate tetrahydrate
composition prepared according to any one
of the claims 1 to 19.

15 21. A process according to claim 1 substantially
as hereinabove defined with reference to examples 1
to 4 inclusive.

22. A zirconium sulfate tetrahydrate composition
prepared according claim 1 substantially as
20 hereinabove defined with reference to examples
1 to 4 inclusive.

INTERNATIONAL SEARCH REPORT

International Application No PCT/AU 87/00344

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) According to International Patent Classification (IPC) or to both National Classification and IPC Int. Cl. ⁴ C01G 25/06, C22B 3/00, 34/14																				
II. FIELDS SEARCHED Minimum Documentation Searched Classification System Classification Symbols IPC C01G 25/06, C22B 3/00, 34/14 Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched AU : IPC as above																				
III. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category *</th> <th>Citation of Document, ** with indication, where appropriate, of the relevant passages **</th> <th>Relevant to Claim No. **</th> </tr> </thead> <tbody> <tr> <td>Y</td> <td>US,A, 1648569 (TRAPP) 8 November 1927 (08.11.27) See column 1 lines 18-30 and Examples 1 & 2</td> <td>(1)</td> </tr> <tr> <td>Y</td> <td>WO,A, 86/04614 (COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION) 14 August 1986 (14.08.86) See claims 1 and 14</td> <td>(1)</td> </tr> <tr> <td>A</td> <td>AU,A, 19187/24 (N.V. PHILIPS' GLOEILAMPENFABRIEKEN) 15 August 1924 (15.08.24)</td> <td>(1)</td> </tr> <tr> <td>A</td> <td>AU,B, 36935/58 (224798) (BRITISH TITAN PRODUCTS CO. LTD) 9 October 1958 (09.10.58)</td> <td>(1)</td> </tr> <tr> <td>A</td> <td>US,A, 3672825 (GAMBALE et al) 27 June 1972 (27.06.72)</td> <td>(1)</td> </tr> </tbody> </table>			Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages **	Relevant to Claim No. **	Y	US,A, 1648569 (TRAPP) 8 November 1927 (08.11.27) See column 1 lines 18-30 and Examples 1 & 2	(1)	Y	WO,A, 86/04614 (COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION) 14 August 1986 (14.08.86) See claims 1 and 14	(1)	A	AU,A, 19187/24 (N.V. PHILIPS' GLOEILAMPENFABRIEKEN) 15 August 1924 (15.08.24)	(1)	A	AU,B, 36935/58 (224798) (BRITISH TITAN PRODUCTS CO. LTD) 9 October 1958 (09.10.58)	(1)	A	US,A, 3672825 (GAMBALE et al) 27 June 1972 (27.06.72)	(1)
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<p>* Special categories of cited documents: 18</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p>																				
IV. CERTIFICATION <table border="1"> <tr> <td>Date of the Actual Completion of the International Search 4 February 1988 (04.02.88)</td> <td>Date of Mailing of this International Search Report (09.02.88) 9 FEBRUARY 1988</td> </tr> <tr> <td>International Searching Authority Australian Patent Office</td> <td>Signature of Authorized Officer J.L. Werner J.L. WERNER</td> </tr> </table>			Date of the Actual Completion of the International Search 4 February 1988 (04.02.88)	Date of Mailing of this International Search Report (09.02.88) 9 FEBRUARY 1988	International Searching Authority Australian Patent Office	Signature of Authorized Officer J.L. Werner J.L. WERNER														
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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON
INTERNATIONAL APPLICATION NO. PCT/AU 87/00344

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document
Cited in Search
Report

Patent Family Members

WO 8604614

AU 53972/86

EP 210236

END OF ANNEX